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Michal Guláš, Costel Sorin Cojocaru, Claudiu Fleaca, Samir Farhat, Pavel Veis, Francois Le Normand

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Synthesis of carbon nanotubes by plasma-enhanced CVD process: gas phase study of synthesis conditions

M. Guláš[1,2,a], C.S. Cojocaru[1], C.T. Fleaca[1], S. Farhat[3], P. Veis[2], and F. Le Normand[1]

[1] Groupe Surfaces and Interfaces, IPCMS, UMR 7504 CNRS, 23 rue du Loess, 67034 Strasbourg Cedex, France
[2] Department of Experimental Physics, FMFI, Comenius University, Mlynská dolina, F2, 84248 Bratislava, Slovakia
[3] LIMHP, Université Paris-13, avenue J.B. Clément, 93430 Villetaneuse, France

Abstract. To support experimental investigations, a model based on Chemkin™ software was used to simulate gas phase and surface chemistry during plasma-enhanced catalytic CVD of carbon nanotubes. According to these calculations, gas phase composition, etching process and growth rates are calculated. The role of several carbon species, hydrocarbon molecules and ions in the growth mechanism of carbon nanotubes is presented in this study. Study of different conditions of gas phase activation sources and pressure is performed.

1 Introduction

Carbon nanotubes (CNTs), firstly observed in 1991 [1] on a negative electrode during electric arc discharge, are considered to be very perspective materials for different applications [2,3]. However, more recently, the Catalytic Chemical Vapor Deposition (C CVD) is believed to be the most fruitful method for nanotube synthesis. Besides the ability to produce high yield of well aligned CNTs [4], the localized [5], low-cost [6] and low temperature [7] growth is possible. Unfortunately the number of defects, due to the low temperature catalytic growth, is also higher and the growth mechanism is not so well described as for the electric arc discharge method and the laser ablation method [5].

Chemical vapor deposition (CVD) is widely used for the manufacturing of coatings, powders, fibers, integrated circuits and composites. Chemical vapor deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase [8]. There are different types and modifications of CVD such as: Atmospheric Pressure Chemical Vapor Deposition (AP CVD), Plasma Enhanced Chemical Vapor Deposition (PE CVD).

In previous works we presented the study of the plasma influence on gas phase mechanism [9] and different CCVD activation modes on the growth of CNTs [10]. The purpose of this paper is to further explore different parameters on the growth of CNTs in the Plasma Enhanced Hot Filament Catalytic Chemical Vapor Deposition (PE HF CCVD). The influence of filament temperature and operating pressure is discussed and confronted with the simulation model.

2 Synthesis and computational model

The Ultra High Vacuum (UHV) CVD chamber used for the synthesis of CNTs and diamond is described in more details elsewhere [10–12]. This reactor allowed performing four different types of deposition synthesis. Thermal CCVD where infra-red halogen lamp was used to heat the substrate, PE CCVD with additional direct-current glow discharge in the gas phase, HF CCVD with tungsten filaments placed above the substrate and a mixture of the two last modes (PE HF CCVD).

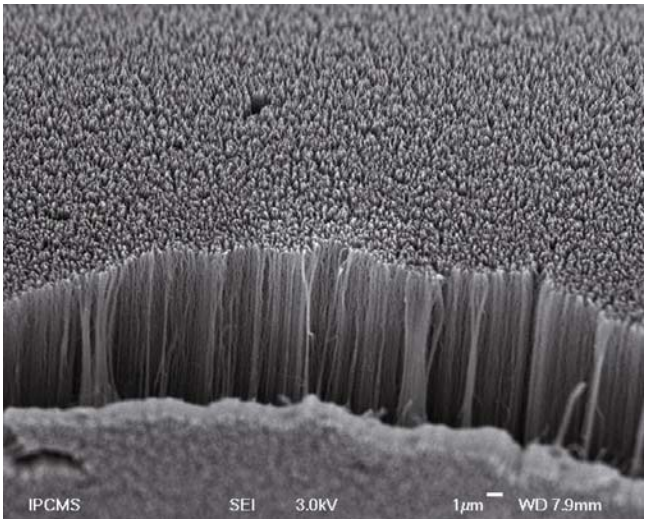
The gas inlet of 100 sccm, mixture of 20 C_2H_2/ 79 H_2/ 1 NH_3, was activated by hot-filaments and glow discharge. The four tungsten filaments were placed two by two above the substrate 5 mm and 10 mm, respectively. Filaments were heated to 1900 K or 2225 K and plasma power $P_p \sim 1$ W was used. The operating pressures of 5 mbar and 10 mbar were investigated.

For the gas phase simulations of PE HF CCVD synthesis of nanotubes, the CHEMKIN [13] software was used. This collection of software consisted of various programs such as: AURORA which allowed the simulation of electrons density, ion density for thermal or non-thermal plasma where temperature of gas T_g differed from temperature of electrons T_e. In the case of the carbon nanotube

formation by a PE HF CCVD process, the incoming gas was activated by hot filaments and the simulation domain lied between the filaments and the plasma, hence the SPIN program was used to simulate this reactor region in (1D) spatial dimension. For the simulations of gas phase chemistry of the $C_2H_2/H_2/NH_3$ mixture, a total of 45 species (29 neutral species and 16 charged species) and more than 200 reactions were used. Surface reaction mechanism was based on the Grujicic model [14] for CVD growth, which had been extended to employ 10 surface carbon and hydrocarbon species (C_xH_y, $2 \geq x > 0$, $5 > y \geq 0$) and cobalt as catalytic nanoparticle. The model equations and reaction schemes for both gas phase and surface mechanism were described in more details in our previous work [9]. It was postulated that the catalytic particle in these conditions, with diameter around a few nanometer, were in liquid form [15]. It was believed that the catalytic growth mechanism of carbon nanotubes was based on the Vapor-Liquid-Solid (VLS) model which was first proposed to explain the growth of carbon nanofibers [16,17]. In this model the carbon feedstock gas decomposed over the catalyst nanoparticle surface. Then carbon dissolved inside the catalyst creating a liquid metal carbide compound, which accumulated until a supersaturation was reached. Then carbon precipitation occurred to form a nanotube [18–20].

3 Results and discussion

It was previously experimentally observed that ideal synthesis conditions in our set-up are as follows: operating pressure of $P = 10$ mbar, inlet gas composition of 100 sccm (20% C_2H_2, 79% H_2, 1% NH_3), filament temperature $T_f = 2200$ K, plasma power $P_p = 1$ W, substrate temperature $T_S = 975$ K and time of growth $t = 15$ min. These conditions are further refereed to standard conditions. The deposited product was examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM images of vertically oriented dense film of synthesized CNTs with bimetallic catalyst (Fe/Co layer of ~1 nm) on TiN /Si(100) and cobalt catalyst on Si(100) are shown in Figures 1a and 1b, respectively. Whatever the substrate and the active catalysts, growth of oriented nanotubes is observed. Experimental growth rates G are ~0.5μm/min in both cases. This is in very good agreement with simulated rate of 0.8 μm/min.



(a)

(b)

Fig. 1. Dense film of CNTs grown on (a) TiN/Si(100) and (b) Si(100). Operating pressure of $P = 10$ mbar, inlet gas composition of 100 sccm (20% C_2H_2, 79% H_2, 1% NH_3), filament temperature $T_f = 2200$ K, plasma power $P_p = 1$ W, substrate temperature $T_S = 975$ K and time of growth $t = 15$ min.

3.1 Effect of the filament temperature

When the filaments were turned off in the same set-up, only few tubular structures were observed [10]. These results triggered studies of different growth conditions. It is expected that not only the on/off status of hot filaments may influence the deposited products, but also different temperatures of filament can bring significant changes. The role of the high temperature filaments $T_f \sim 2000$ K is mainly to deliver a large decomposition of molecular hydrogen H_2 to atomic hydrogen H which plays a main role in etching of the surface and in preventing amorphous carbon synthesis [9]. Atomic hydrogen can be produced also by the primary plasma through electron impact dissociation of H_2 [21]. However for a sufficient H production by plasma reactions, a plasma power much higher than 1 W is needed. Another way to obtain a sufficient amount of atomic hydrogen require starting from a different gas inlet, however this is not the purpose of our study.

The experimental study and modeling is performed at $T_f = 1900$ K where the hydrogen decomposition is expected to be lowered compared to $T_f = 2200$ K. In Figure 3 is shown the SEM image of the as-prepared sample. It is obvious that a rare occurrence of CNTs is acquired. The growth rate is experimentally estimated to

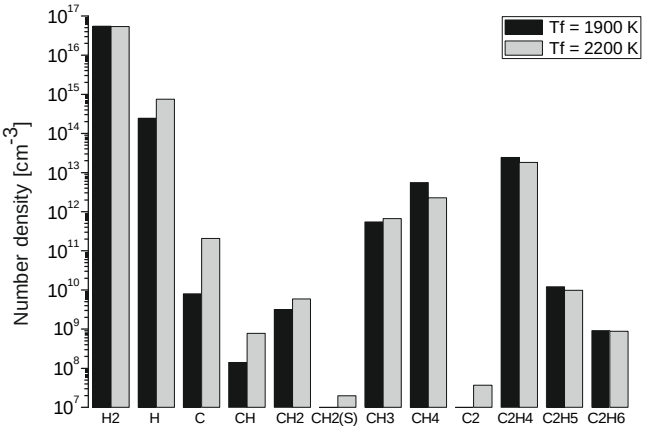


Fig. 2. Number densities of gas phase species close to the surface in PE HF CCVD with filament temperature 1900 K and 2200 K, respectively.

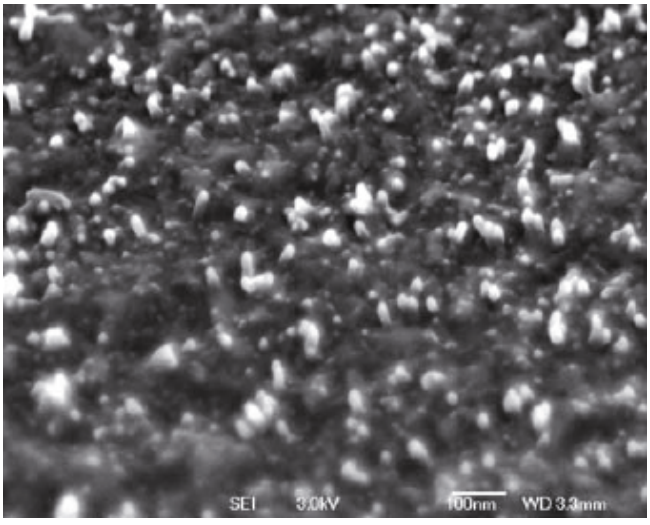


Fig. 3. Deposition of tiny carbon nanotubes on Si(100). Same experimental conditions as in Figure 1, except different temperature of filaments $T_f = 1900$ K.

$G \sim 1$ nm/min, three orders of magnitude lower. This slow rate of CNTs production can be clearly explained by our simulation model. The 300 K difference of filament temperature does not cause significant change to the atomic hydrogen abundance ($[H]_{2200K} = 7.4 \times 10^{14}$ cm^{-3}, $[H]_{1900K} = 2.4 \times 10^{14}$ cm^{-3}), nevertheless relevant variations of carbon and hydrocarbon species can be calculated (Fig. 2). A decrease of the filament temperature implies only a slight increasing of the acetylene dissociation, because of the higher stability of C_2H_2 at higher temperatures. However the products of the dissociation are different. Concentration of hydrocarbons with a high hydrogen content increased, like CH_4, C_2H_4, $C_2H_5$and C_2H_6. They are expected to be responsible for the deactivation of catalytic particle [22]. On the other hand, abundance of carbon species (C, C_2) and hydrocarbons with low hydrogen content (CH, C_2H) decrease significantly.

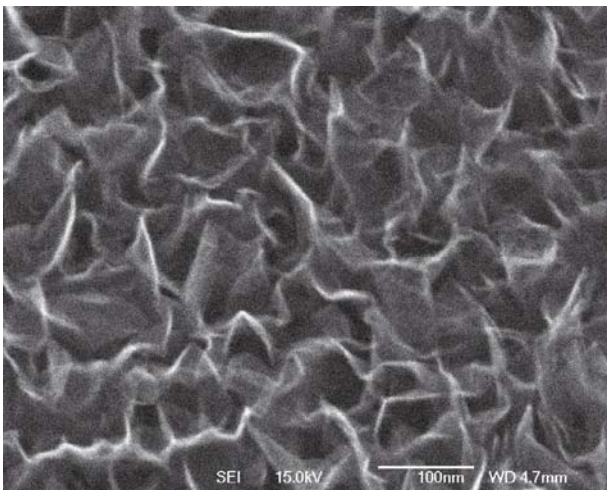


Fig. 4. Carbon nanowalls produced in operating pressure of 5 mbar, the rest experimental conditions are the same as in Figure 1.

This leads to conclusion that different decomposition paths occur, or that due to a lower thermal energy decomposition of higher hydrocarbons was not complete. The abundance of carbon monomers decrease by around two orders of magnitude (from 10^{11} cm^{-3} with $T_f = 2200$ K to 10^9 cm^{-3} with $T_f = 1900$ K), the dimer C_2 decreases by one order of magnitude (10^7 cm^{-3} and 10^6 cm^{-3}, respectively), and CH, C_2H species decrease around a half order of magnitude. It should also be mentioned that no significant changes are observed in the concentration of nitrogen-containing species and charged species.

3.2 Effect of the operating pressure

No carbon nanotubes were synthesized, when standard conditions were kept, except an operating pressure set at 5 mbar. Also Bratescu et al. [23] are not able to produce CNTs below 10 mbar using a PE CCVD process, however it should be noted that they use different gas precursors. Reversely at 5 mbar carbon nanowalls [24] are grown (Fig. 4). They are grapheme sheets grown vertically from the substrate. Regarding the gas phase simulation, no significant changes of hydrocarbon species abundance are observed at 10 mbar and 5 mbar, respectively. Of course the number density decreased, due to the pressure drop, however mole fractions are almost the same. However, a strong change of the atomic hydrogen concentration can be measured. While in synthesis at 10 mbar the mole fraction of atomic hydrogen reaches 10% of the gas mixture close to the substrate, at an operating pressure of 5 mbar the mole fraction of atomic hydrogen is close to 23%. Thus it is believed that hydrogen atoms play a key role in stabilizing unclosed graphene sheets, possibly by providing hydrogen to the dangling bonds at the edge of the graphene sheets. These results are confirmed by Hiramatsu et al. [25]. They also produce nanowalls by PE CVD only with the assistance of hydrogen radical injection to the reactor.

4 Conclusion

Different changes in the deposited product or the growth rate are explained by combining SEM and TEM observations with gas phase investigations. Thus it is shown that by decreasing the hot filaments temperature in the PE HF CCVD process, drastic decrease in the highly dehydrogenated hydrocarbon in the gas phase is calculated and this could explained the drop of the growth rate. By decreasing the pressure from 10 to 5 mbar, carbon nanowalls instead of carbon nanotubes are deposited. This could be relied with a large increase of the atomic hydrogen fraction.

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